IMPURITIES IN HIGH MOLECULAR WEIGHT AMINE PRODUCTS

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The analysis of high molecular weight amines and of such products as the amine acetates is rather difficult, particularly when impurities are to be determined. There are three reasons for the difficulty. First, the amines are complex mixtures obtained from natural products, such as animal and vegetable fats. Thus, they will contain some of the sterols originally present in the fat. Second, the chemical properties of the constituent compounds are rather similar. The probable components can be deduced from a typical commercial method of synthesis (Armour, 1948). This consists of: hydrolysis of the fat, separation of the fatty acid, formation of the amide by reaction with ammonia, dehydration of the amide to form the nitrile, hydrogenation of the nitrile to the amine, and finally the reaction of the amine with acetic acid, if desired. The last step can lead to the formation of N-alkyl acetamides by dehydration of the amine acetate. Thus, in addition to primary, secondary and tertiary amines, we may expect to find nitriles, amides, N-alkylacetamides, and sterols. The third cause of difficulty in analysis is that the high molecular weight amines and their salts are surfactants, with the result that solutions foam to a great extent, and precipitates are frequently kept in suspension. For example, stearic acid will precipatate as lead stearate from 70 percent aqueous acetone upon the addition of lead acetate. However, no precipitate is obtained in the presence of large amounts of octadecylamine acetate.

The obvious solution to the difficulty is the removal of the major portion of the amine, and to analyze for the impurities remaining in the residue. The following are chemical means of separation and analysis which are offered as a partial solution to the problem:

A. *Amine content*

The amine number is determined by the usual method of titrating with standard percholoric acid in glacial acetic acid (Terry *et al.*, 1952). The end point should be determined by a potentiometric method using a glass-electrode pH meter, since indicators may give shifting end points.

The manufacturer is usually able to supply an approximate average molecular weight for the amines present in the commercial products. This molecular weight, together with the amount of standard acid used, enables one to calculate approximately the weight of amine present in the sample.

Allowance must be made for the fact that usually primary, secondary and tertiary amines are all present. If necessary these can be determined by standard procedures (Wagner *et al.*, 1947).

B. *Removal of the amine*

The amines themselves are the most basic constituents which are expected to be present in commercial preparations of high molecular weight amines. This suggests that the basic properties can be used to separate the amines from the other compounds. Considerable experimentation led to a usable procedure for removal of the amine.

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MATERIALS AND METHODS

The materials necessary for the analysis are pure benzene, pure acetone, a glass-electrode pH Meter, and a standard oxalic acid solution. The latter is 1.000 molar, and is prepared by dissolving 126.1 g. of $H_2C_2O_4 \cdot 2H_2O$ in almost a liter of acetone, and diluting to a liter after the cold solution has attained room temperature. A saturated solution is about 1.5 molar.

A sample of amine or amine acetate weighing 3.00 g. is dissolved in 100 ml. of benzene. Slight warming will aid the process, and is sometimes necessary for the more insoluble materials. From the amine number, A, of the amine product a calculation is made of the theoretical amount of oxalic acid solution needed to precipitate the amines as the amine acid oxalate.

$$V = \frac{3.00\ A}{56.11}$$

This volume of oxalic acid solution, plus 1 to 2 percent excess, is added dropwise from a burette, with constant stirring. (Oxalic acid is insoluble in benzene and will precipitate if the acetone solution of oxalic acid is added to pure benzene. The slow addition and stirring are intended to disperse the oxalic acid so that it reacts with the amine.) After standing one-half hour or more to insure complete reaction, the bulky gelatinous precipitate is filtered by suction and washed with benzene. A fine-porosity fritted glass buchner funnel is quite satisfactory. A covering of a filter aid, such as "Super Cel," will prevent plugging of the pores, and make cleaning of the funnel easier. The benzene is evaporated to "dryness" by gentle warming in a casserole or evaporating dish. The residue is considered "dry" when no odor of benzene or acetic acid is detectable.

The following materials were used: purified hexadecylamine acetate; a standard sample containing 95 percent hexadecylamine acetate, 3.00 percent Arneel 18D (chiefly stearonitrile), 1.00 percent hexadecylacetamide, and 1.00 percent stearamide; Armeen 16D (chiefly hexadecylamine); Armeen 2HT (chiefly dioctadecylamine); Armac HT (chiefly octadecylamine acetate); Armac 2HT (chiefly dioctadecylamine acetate), Alamac 26D (chiefly octadecylamine acetate); and Rosinamine D (chiefly dehydroabietylamine).

The purified hexadecylamine acetate was prepared by adding 144 g. of commercial hexadecylamine to about 300 ml. of benzene, adding 36 g. of glacial acetic acid, warming to 45–50° C to dissolve all of the material, and filtering the precipitate after cooling to 20–25° C. (It should be noted that the heat of reaction of the amine and acetic acid is rather high.) The product was recrystallized twice more from about 300 ml. portions of benzene, left in the air until the odor of benzene disappeared, then dried in a desiccator over magnesium perchlorate. Four samples, titrated with standard perchloric acid, gave an average molecular weight of 299.7 with an average deviation of 0.4. The molecular weight of hexadecylamine acetate is 301.5. The low apparent molecular weight can be attributed to a slight loss of acetic acid. The melting range was 77.5–79.0° C, with a slight sintering before this temperature.

The standard hexadecylamine acetate was prepared by melting 25.65 g. of hexadecylamine acetate in a round-bottom dish, quickly dissolving 0.81 g. of Arneel 18D, 0.27 g. of N-hexadecylacetamide, and 0.27 g. of stearamide, then rapidly cooling the mixture with constant stirring and milling with a spatula until quite solid. Titration showed an apparent molecular weight of this amine-containing material to be 313.7 ± 0.5, compared to the expected value of 314.7. Again the deviation can be attributed to a slight loss of acetic acid.

The N-hexadecylacetamide was prepared by refluxing hexadecylamine with an excess of acetic anhydride in the presence of acetic acid, adding the mixture to ice, then recrystallizing the dried product three times from benzene.

The stearamide was obtained from Eastman Kodak Co.

DISCUSSION

Results for several materials are given in table 1. It can be seen that a small amount of amine may be carried through in solution in the benzene, particularly in the case of very high molecular weight straight-chain primary and secondary amines. Therefore, the procedure should be reasonably standardized so as to insure that the same amount of amine is present after the evaporation of the filtrate. This amine is determined by titrating samples of the residue with standard perchloric acid in glacial acetic acid. The amine is assumed to be present as the amine acid oxalate. It can be seen from the table that at least 97 percent of the amine is removed by one treatment with the oxalic acid.

TABLE 1

Residues from 3 g. of amine products oxalic acid-bensene procedure

Material	Wt. of Residue	Average deviation	% of amine acid oxalate in residue	No. of samples
Hexadecylamine acetate	0.005	0.002	0	4
Standard hexadecylamine acetate	0.148	0.003	0	6
Rosinamine D*	0.164	0.003	0	6
Armeen 16D+	0.072	0.02	2	2
Armeen 2HT+	0.34	0.01	27	2
Armac TD+	0.26	0.03	10	3
Armac 2HT+	0.27		24	2
Alamac 26D±	0.26	0.03	10	4
Alamac 26D, ± pure sample	0.11	0.01	17	2

*Distilled sample, courtesy Hercules Powder Company
+Courtesy of Armour and Company
±Courtesy of General Mills

If desired, the precipitate of amine acid oxalate can be dissolved by heating in glacial acetic acid, and the amine content determined by titrating with the standard perchloric acid.

The limits of the amounts of impurities which can be isolated by this method may be deduced from known solubilities. At room temperature 100 ml. of benzene will dissolve 90 g. of stearonitrile (Ralston, 1948), or 0.35 g. of Armid HT, which contains about 75 percent stearamide and 25 percent palmitamide (Armour, "Armids"). An experiment showed that, at 30° C, 100 ml. of benzene will just dissolve a mixture of 0.15 g. of N-hexadecylacetamide and 0.15 g. of stearmide. Cholesterol is soluble in benzene to the extent of 12.5 g. per 100 ml. at 20° C (Seidell, 1941). The method will thus isolate about 5 percent of amides and N-alkylacetamides. Very few commercial preparations can be expected to have this much amides or N-alkylacetamides. There is no practical limit to the amount of nitriles and sterols which can be isolated.

The efficiency of recovery of non-amine material is shown by the results for

the standard hexadecylamine acetate mixture. The sample contained 5.00 percent of impurities, and an average of 4.93 percent were isolated in the residue.

The results for the various commerical samples are not intended to be definitive, but to indicate the applicability of the method.

C. *Determination of nitriles*

Nitriles can be easily hydrogenated to amines, and the amines can be titrated quite accurately with standard perchloric acid in glacial acetic acid. It was demonstrated that nitriles can be quantitatively hydrogenated in glacial acetic acid by the use of a platinum catalyst (Adams *et al.*, 1928).

MATERIALS AND METHODS

The materials necessary for the nitrile analysis are pure acetic acid, platinum catalyst, pure hydrogen, Parr hydrogenator equipped with shaker, and standard 0.1 normal perchloric acid in glacial acetic acid. The latter is prepared as before.

TABLE 2

Nitriles in amine products

Material	%Nitrile	Av. dev.	No. of samples
Standard Hexadecylamine acetate	2.92	0.16	4
Rosinamine D	0.60	0.06	3
Alamac 26D	3.8	0.3	2
Same, purified sample	1.7	0.3	2
Armac TD	5.1	0.3	2

A sample containing 0.2 to 5 millimole of nitrile is dissolved in about 50 ml. of glacial acetic acid, 0.05 g. of the platinum catalyst added, and the material hydrogenated by shaking in an atmosphere of hydrogen for three hours at 40–50 psig. The resultant solution (with suspended catalyst) is transferred quantitatively to an appropriate flask and titrated with the standard perchloric acid. A potentiometric titration using a pH meter is preferred to the use of indicators. A blank is run on a separate sample containing the nitrile. The increase in basicity of the sample upon hydrogenation corresponds to the amount of nitrile originally present in the sample.

A sample of adiponitrile obtained from Eastman Kodak Company showed an apparent degree of completion of 99.5 percent. This is assumed to represent the purity of the sample. A commercial sample of mixed nitriles (Arneel TD, chiefly stearonitrile) showed 99 percent completion. This is within the limits of error of the purity and average molecular weight of the sample as calculated from data supplied by the manufacturer (Armour, "Arneels"). Stearamide and N-hexadecylacetamide were shown to be inert to hydrogen under these conditions. Raney nickel also may be used, but the end point in the titration is difficult to obtain.

This method was applied to the residues from the oxalic acid-benzene treatment of commerical amine products, and the previously described standard sample containing 3.00 percent nitrile. When information on the molecular weight of the nitrile was not available, its molecular weight was assumed to be four units less than the average molecular weight of the primary amine present in the original sample. The results are given in table 2.

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